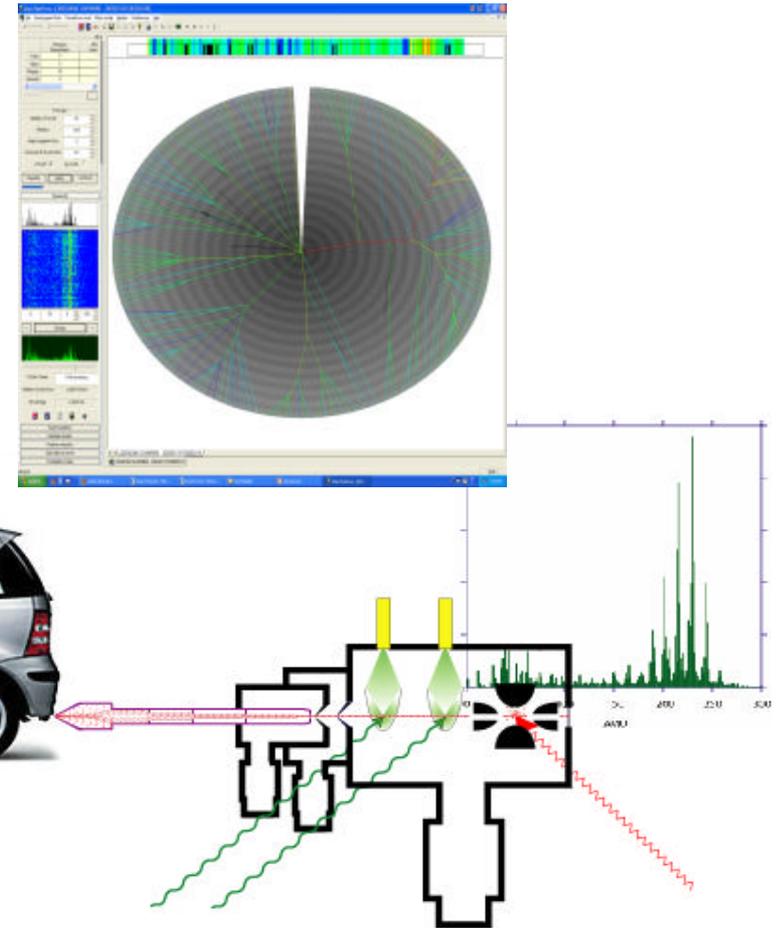
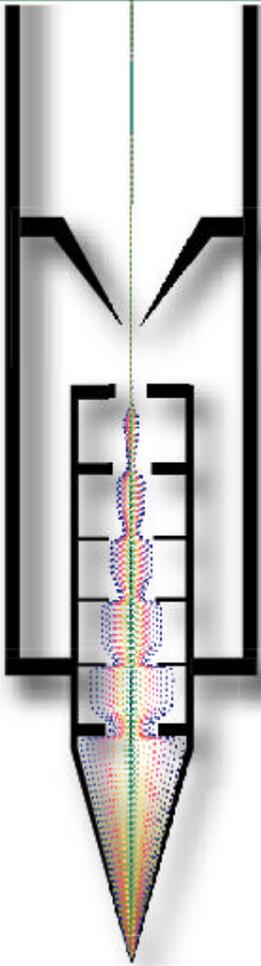


# Real Time Tailpipe Emission Measurements



A. Zelenyuk, D. Imre PNNL

J. Wegrzyn, J Wang, G. Senum BNL

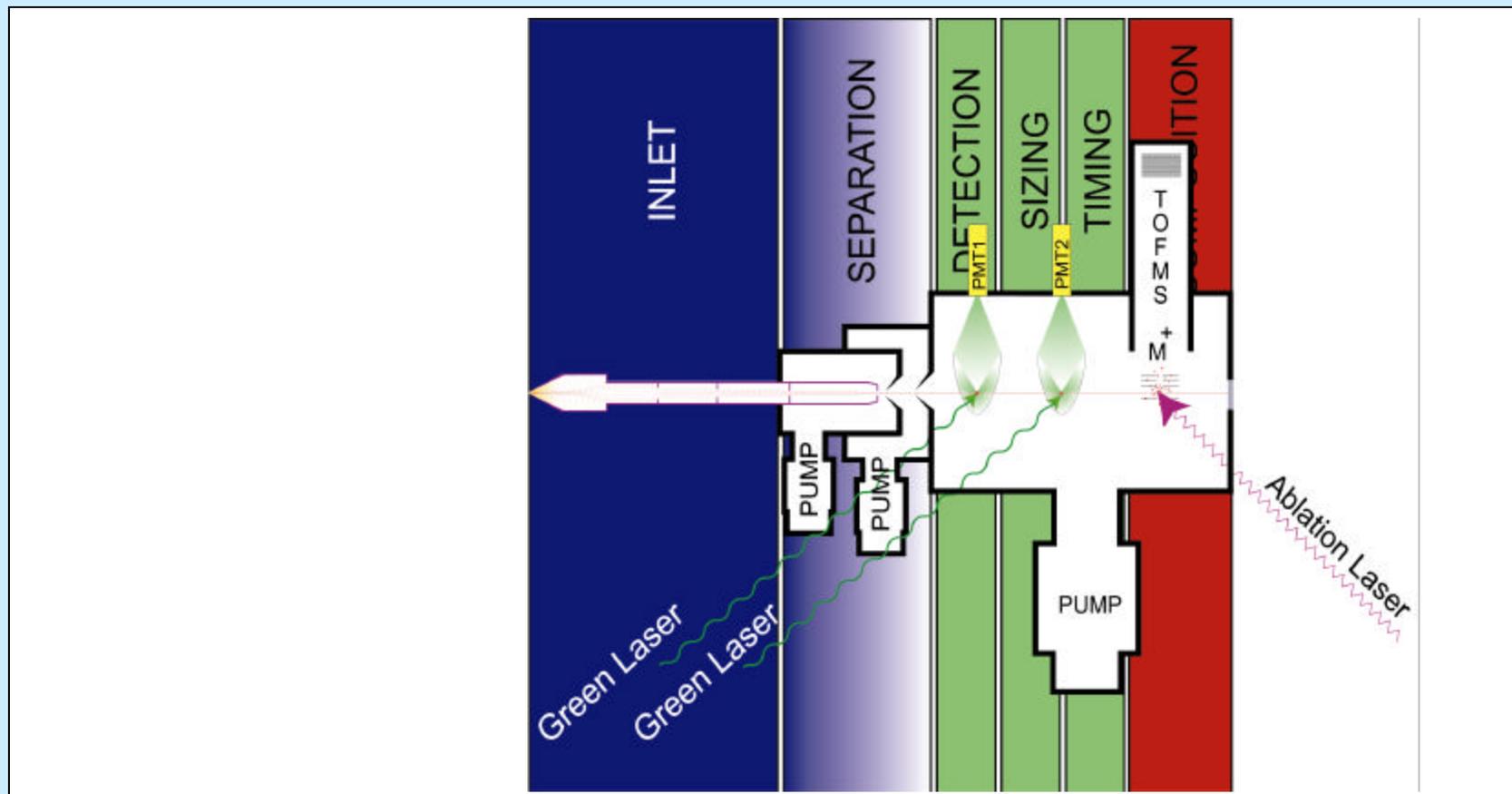
D. Edwards, S. Huff, S. Lewis, J. Storey ORNL/NTRC

# OUTLINE

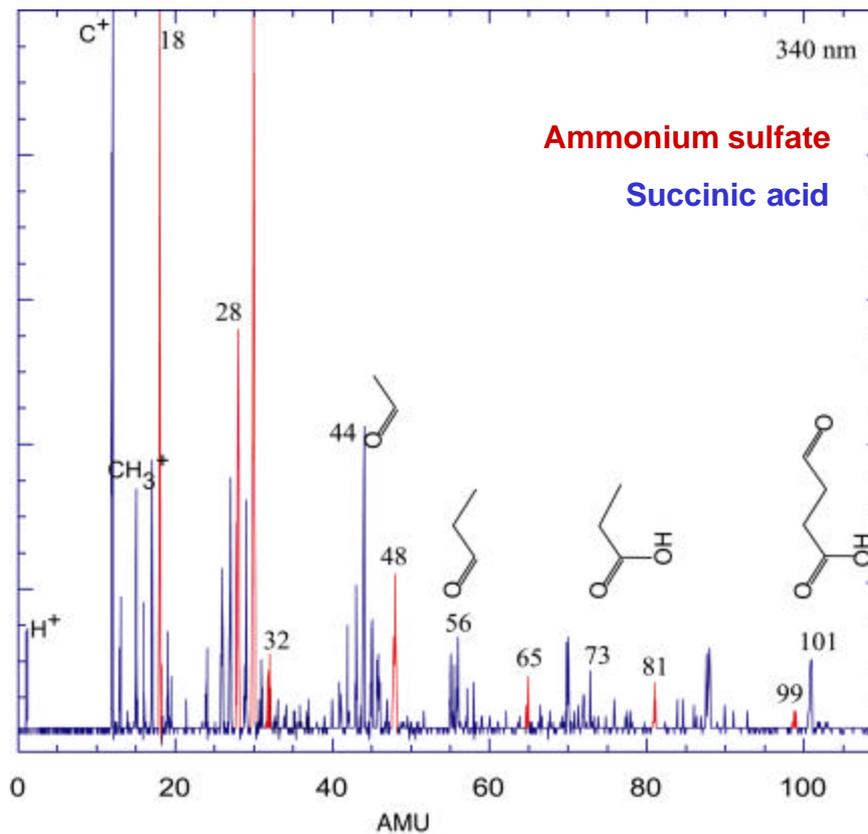
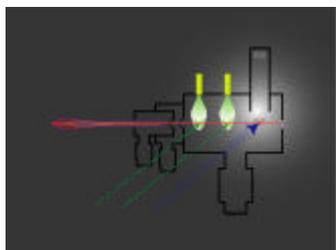
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- **Single particle mass spectroscopy**
  - **Data mining and visualization**
  - **Results from NTRC on a 1.7L Mercedes Diesel Engine**
  - **Future instrument SPLAT II**
  - **Going back to NTRC**
-

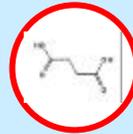
# Single Particle Mass Spectrometry: Basics



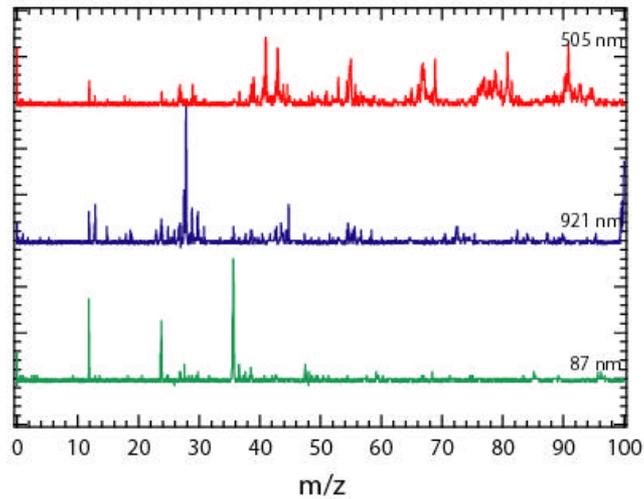
# SPLAT-MS can identify different components of mixed aerosol



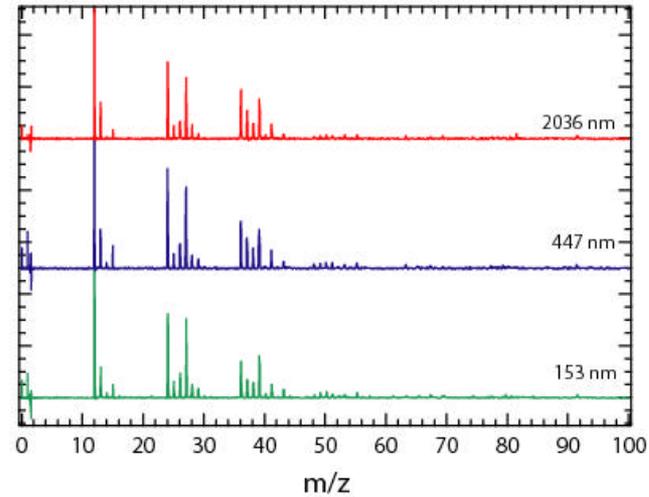
# Separating Ablation into Evaporation Followed by Ionization Greatly Improves the Spectra



## PURE SUCCINIC ACID PARTICLES

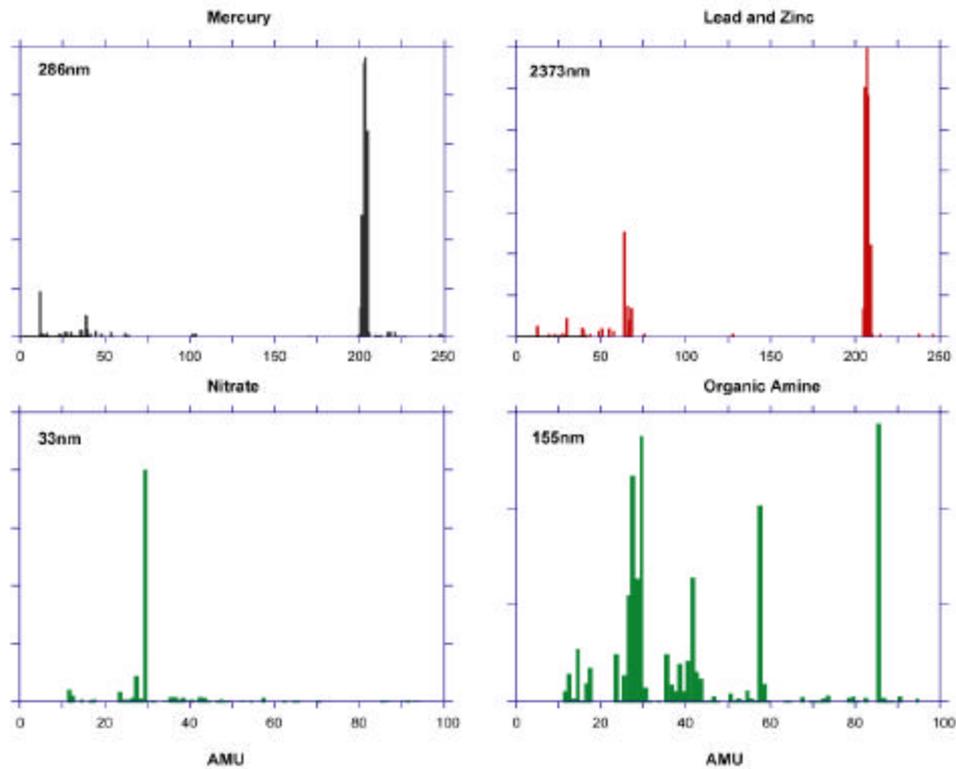


Excimer Laser Only

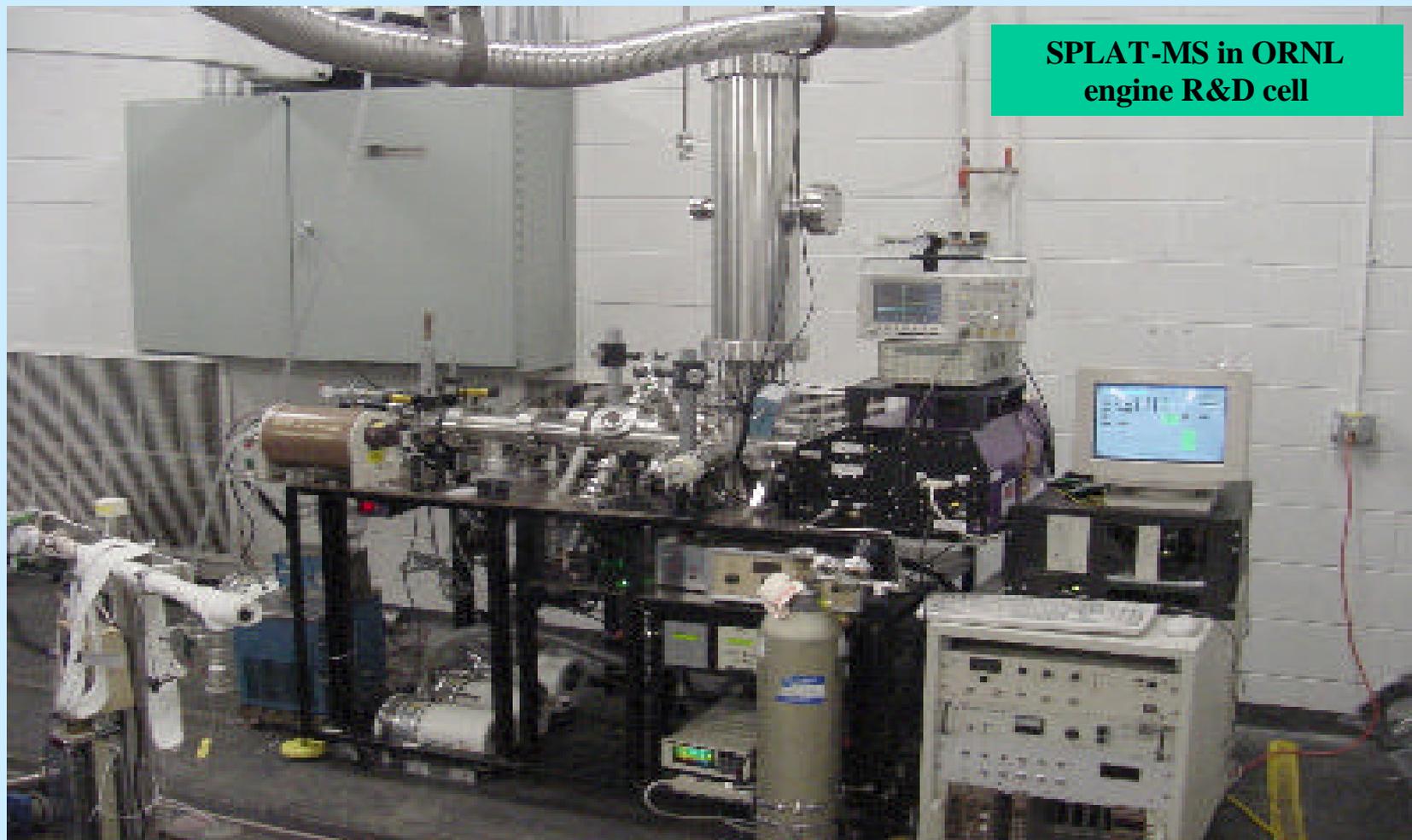


CO<sub>2</sub> and Excimer Laser

# 4 little Particles from Oak Ridge

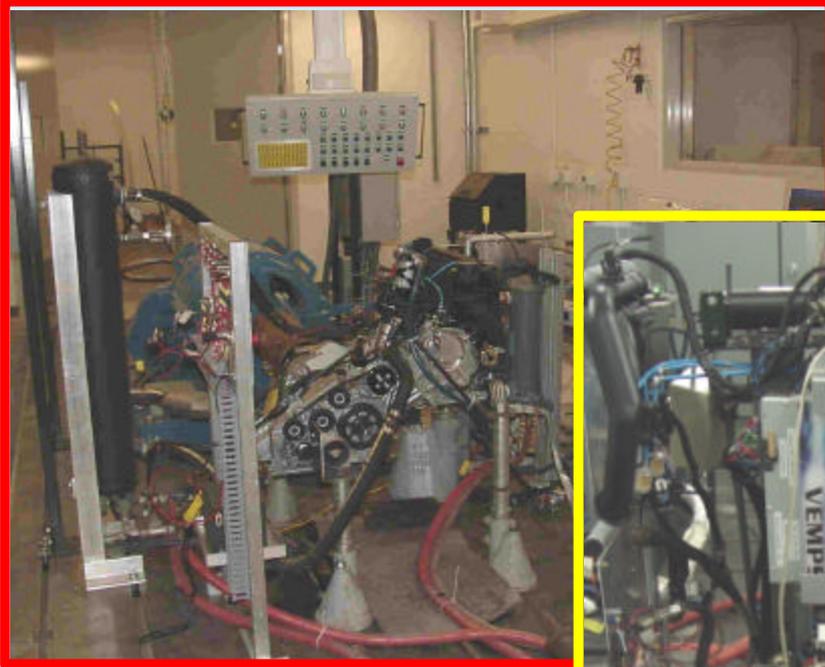


# A Study of LD Diesel at ORNL with SPLAT-MS Feb. 2003



# Mercedes Engine and Motoring Dynamometer at NTRC Cell 2

**New Mercedes 1.7L and motoring dyno**



**Control Room**



**Full-Pass Controller  
Developed with Ricardo**



# Summary of the Experiments

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- Measurements of exhaust particle size, density and composition were performed under variety of operating conditions:
    - Changed loads and RPM
    - LTC/EGR
    - ECD-1 and oxygenate fuels
    - Changed injection sequence and timing
    - Pre and post catalyst
  - Acquired spectra for ~500,000 particles – large dataset!
  - Used high dilution to avoid sampling artifacts
  - Use an IR-UV scheme
-

# SpectraMiner

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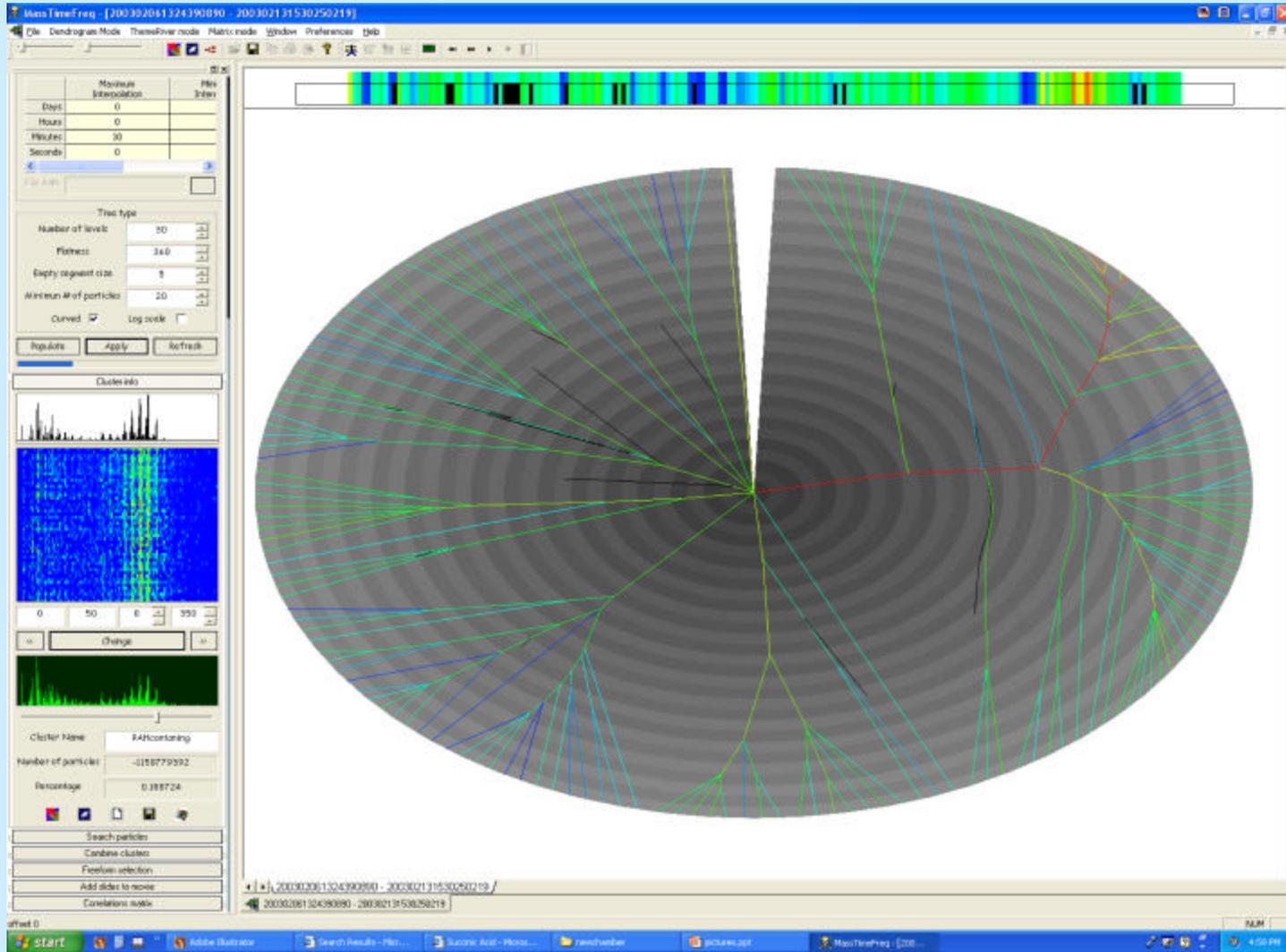
## Let's Take a Look at the Data

Peter Imerich

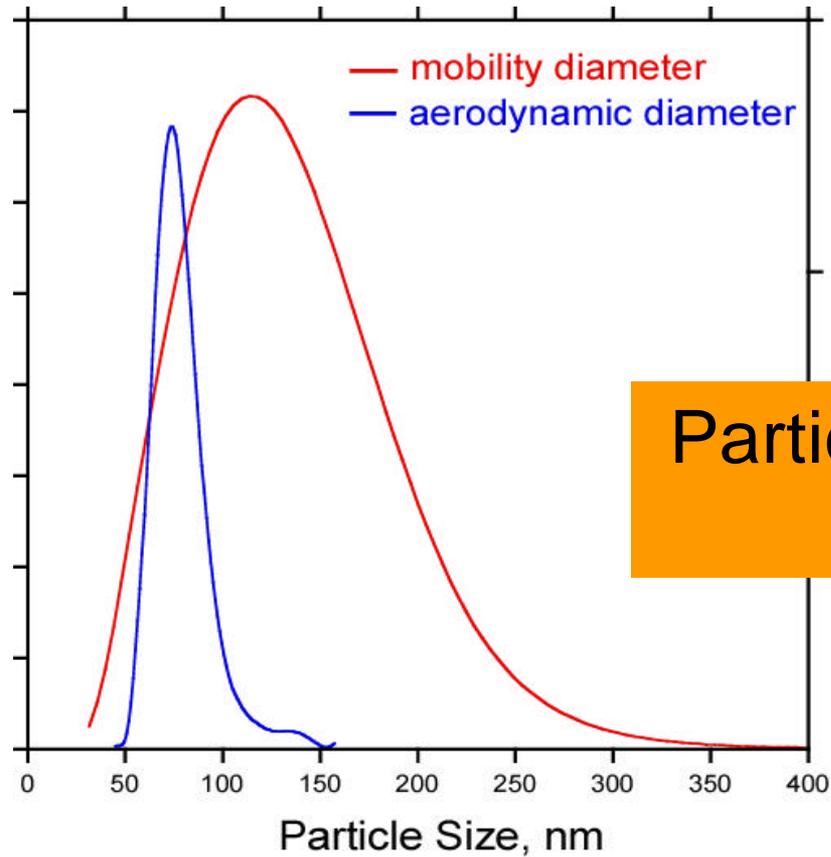
Wei Zhu, Bin Xu, Klaus Muller

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# The Dendrogram or Classification Tree

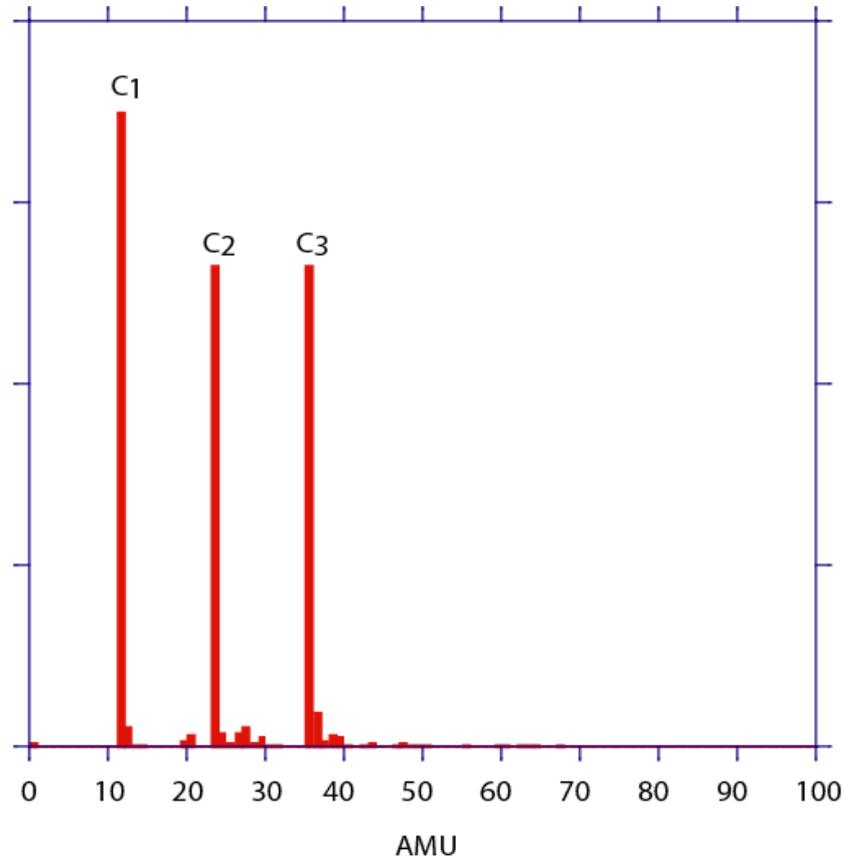


# The Diesel Exhaust Challenge to Particle-MS

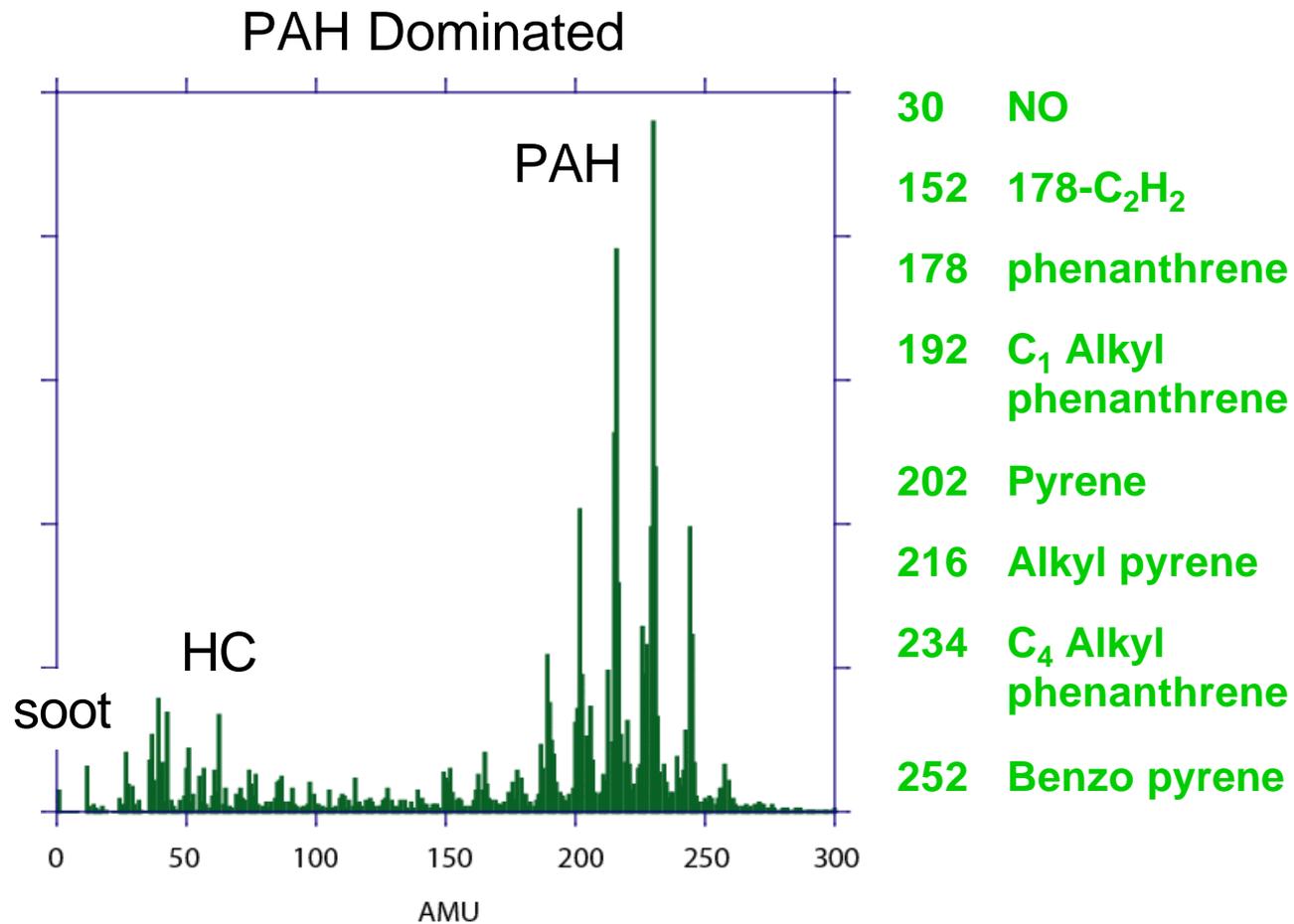


Particles are Very  
**Small**

# Soot Particles are Most Prevalent

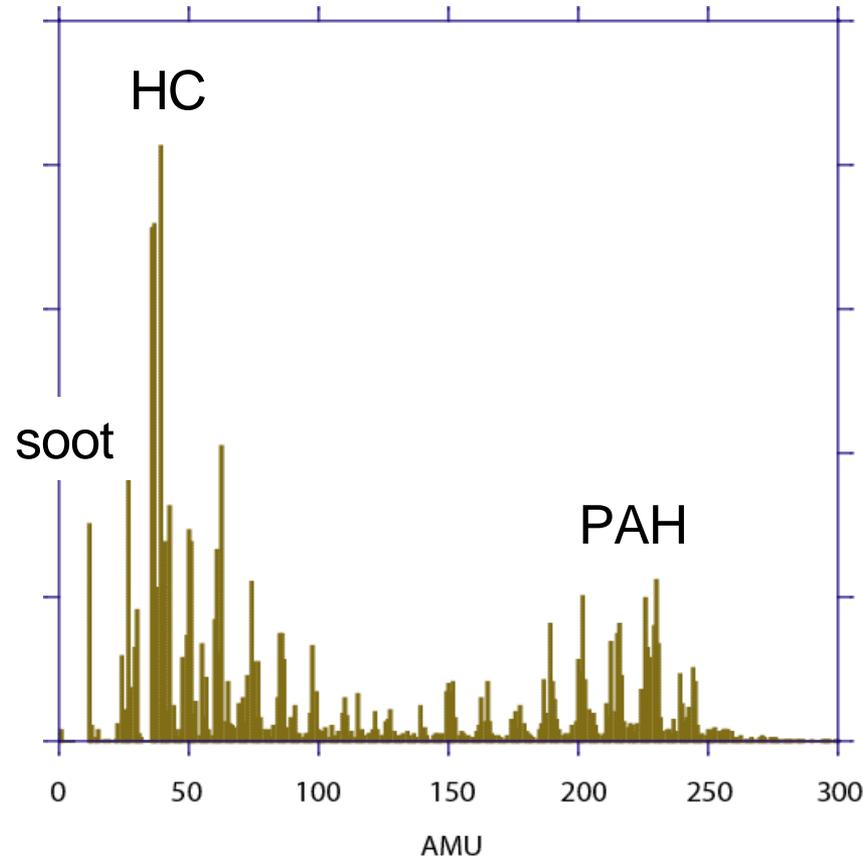


# PAHs Volatilize from Particles using Laser Heating

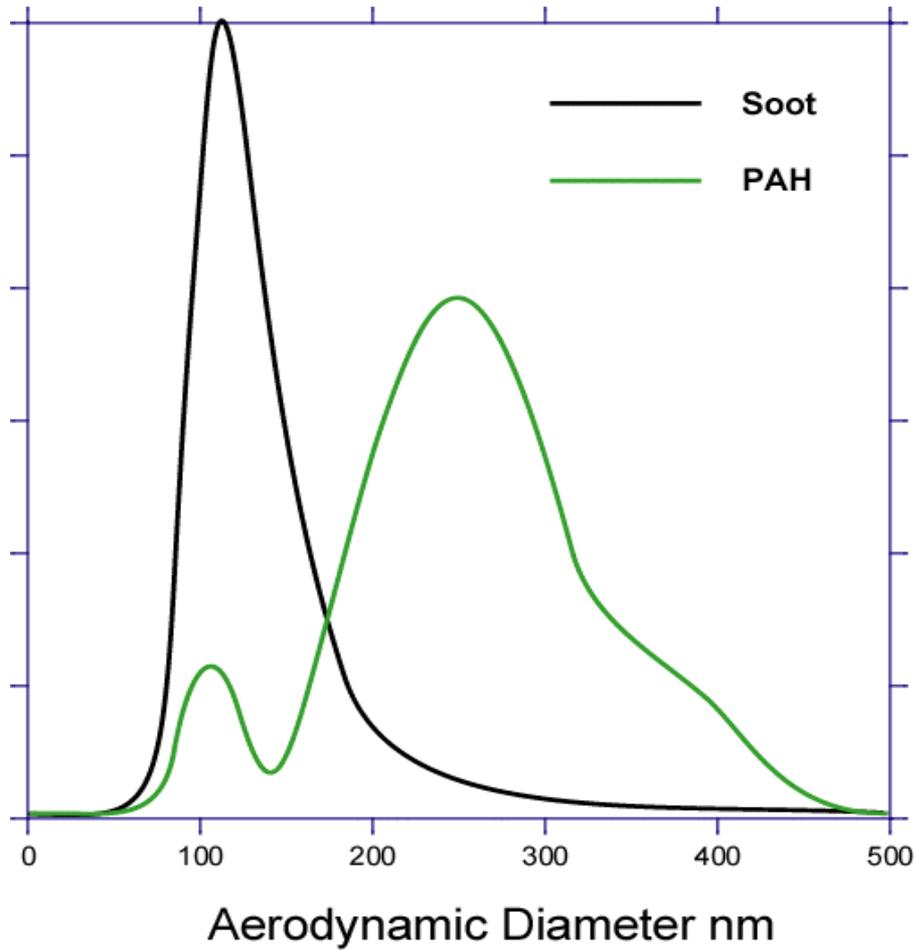


# Unburned and Partially Oxygenated Fuel Volatilize from Particles using Laser Heating

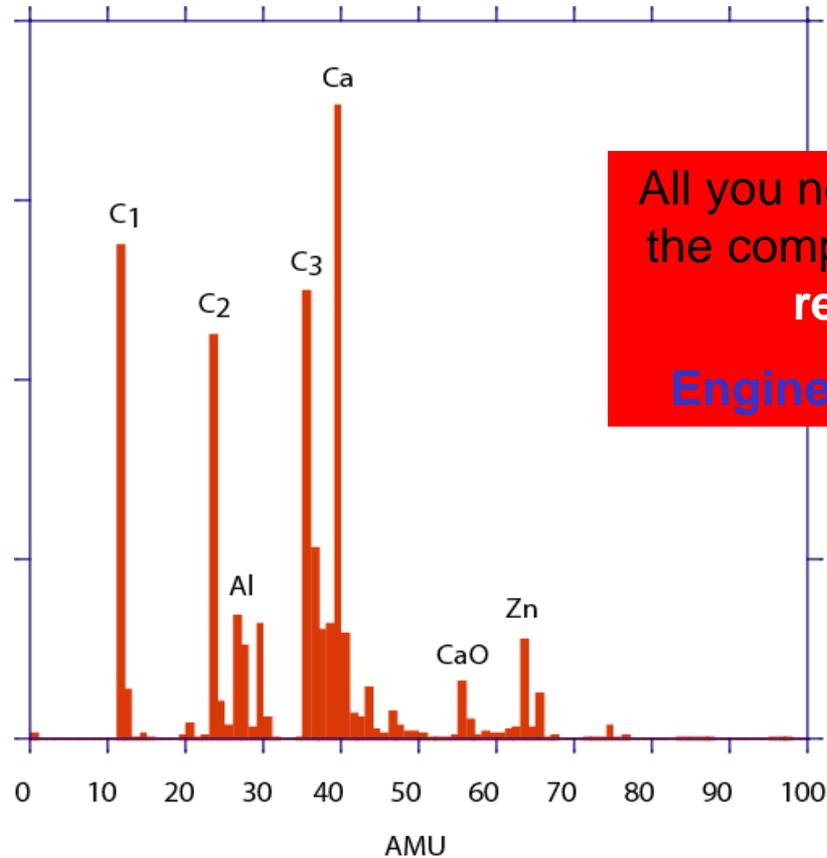
Partially oxygenated hydrocarbons soot and PAH



# Where are the PAHs



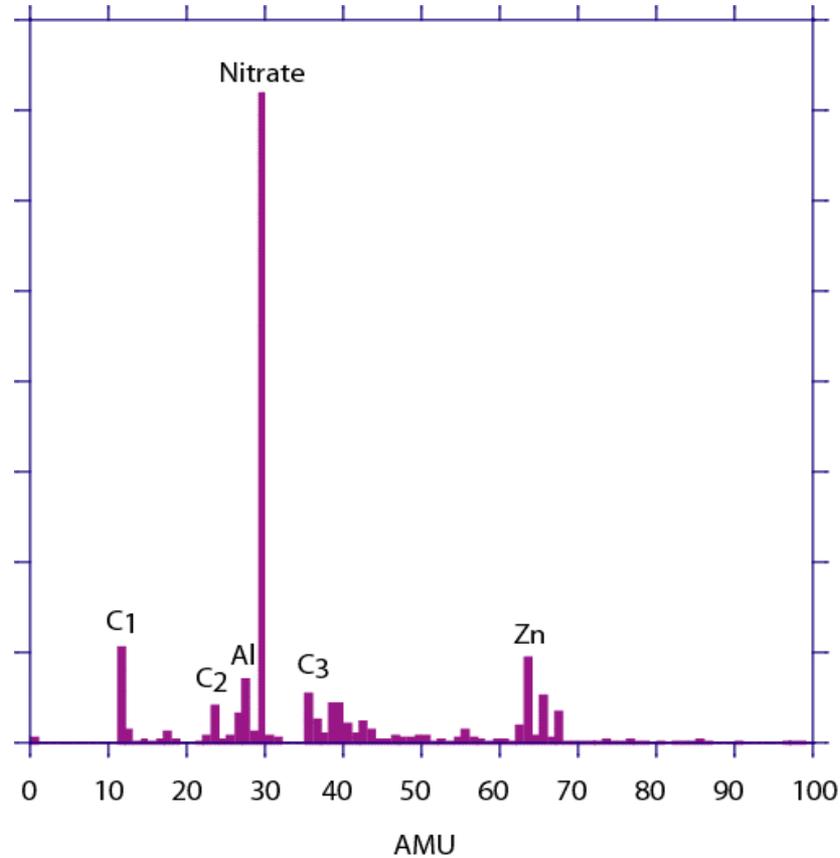
# At Rated Speed, Oil Components and Engine Wear and Tear Appear Products Appear in Particles



All you need is to watch  
the computer screen in  
**real-time**

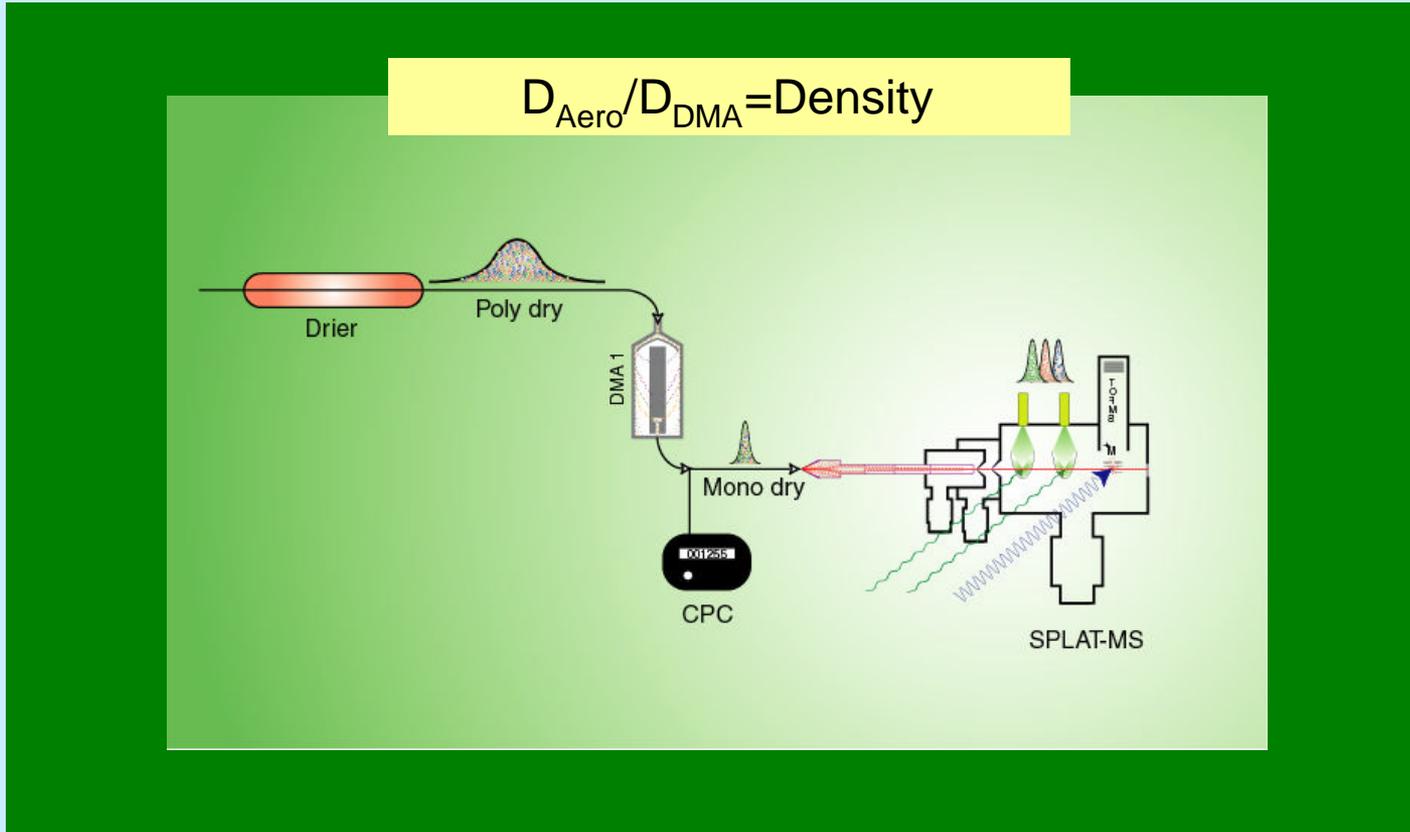
**Engine diagnostics**

# A Small Fraction of Particles Contain Significant Amounts of Nitrates



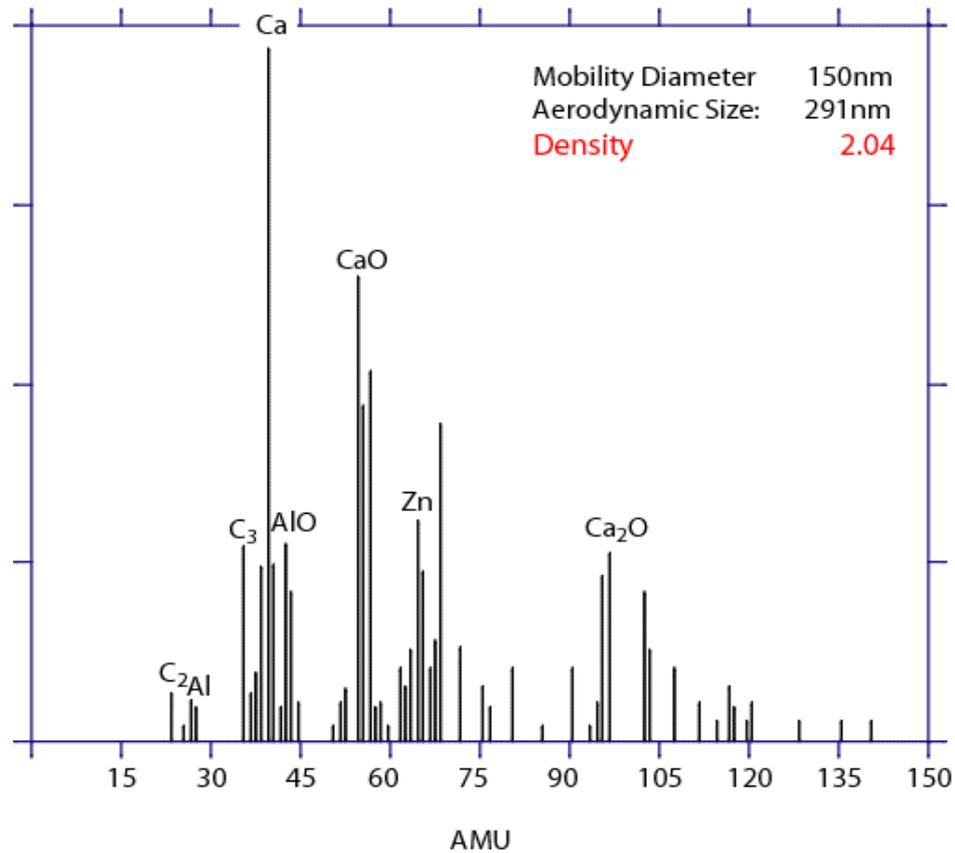
# Size, Composition & Density

## Using SMPS to Feed Particles to SPLAT-MS



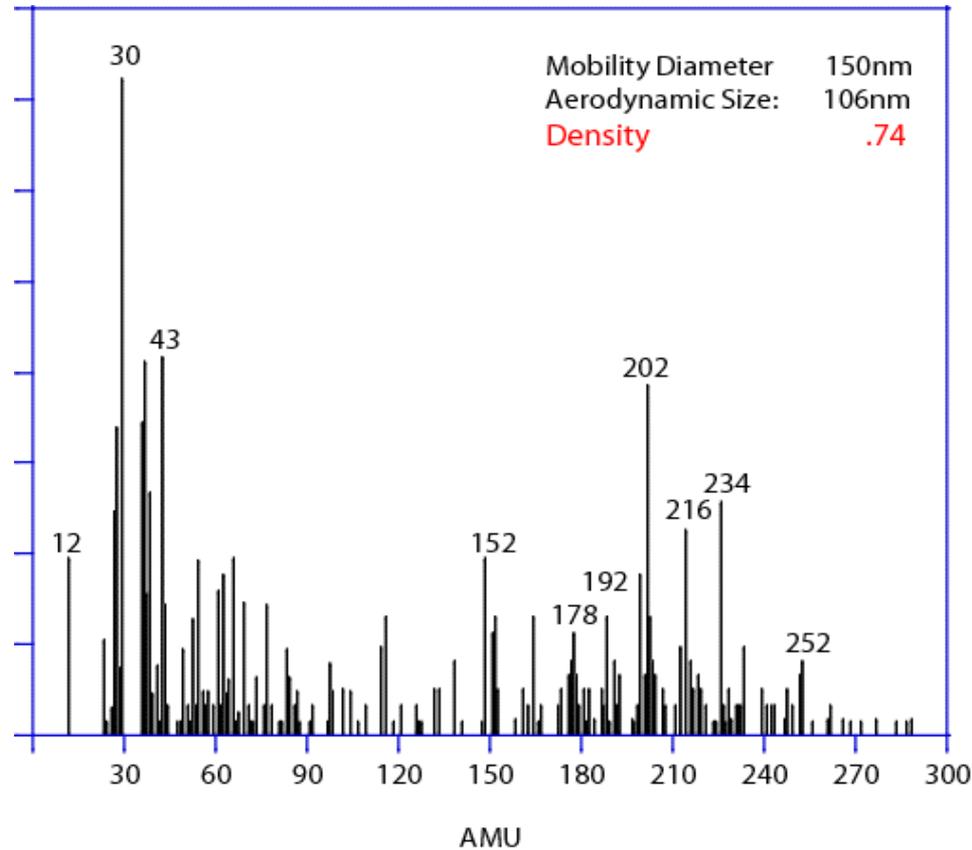
# Particle Density Depends on Composition

## Lube Components and Engine Wear and Tear



# Density Depends on Composition

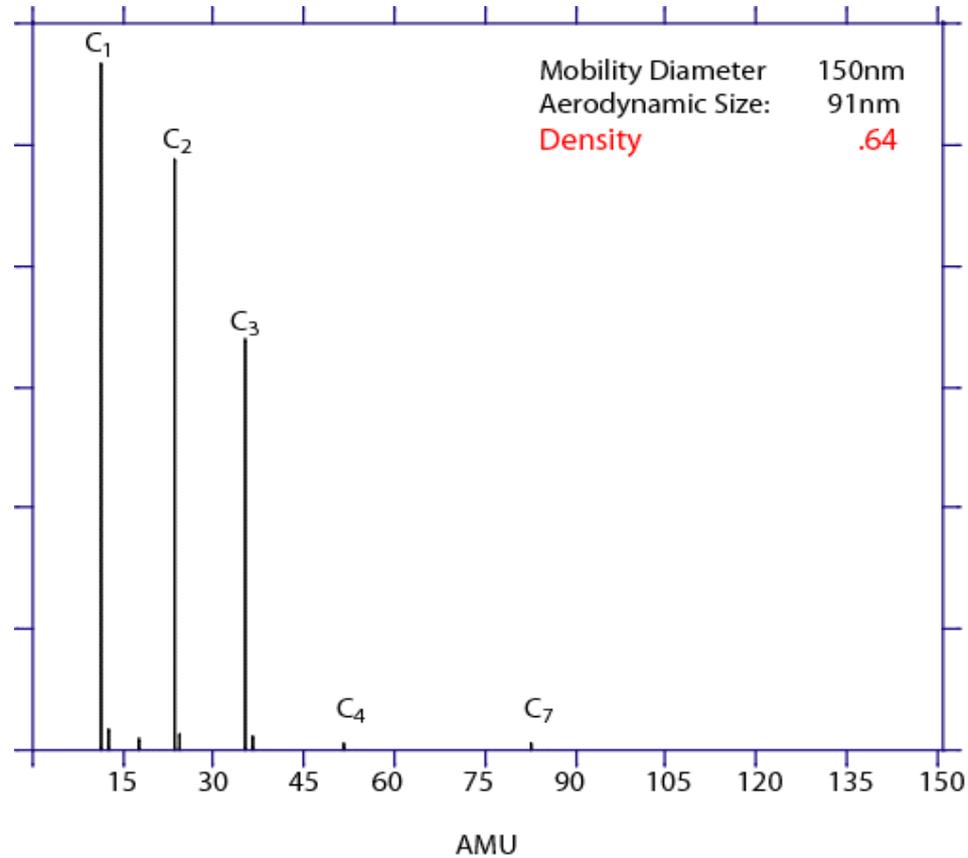
## PAHs



|     |                                   |
|-----|-----------------------------------|
| 30  | NO                                |
| 152 | 178-C <sub>2</sub> H <sub>2</sub> |
| 178 | phenanthrene                      |
| 192 | C <sub>1</sub> Alkyl phenanthrene |
| 202 | Pyrene                            |
| 216 | Alkyl pyrene                      |
| 234 | C <sub>4</sub> Alkyl phenanthrene |
| 252 | Benzo pyrene                      |

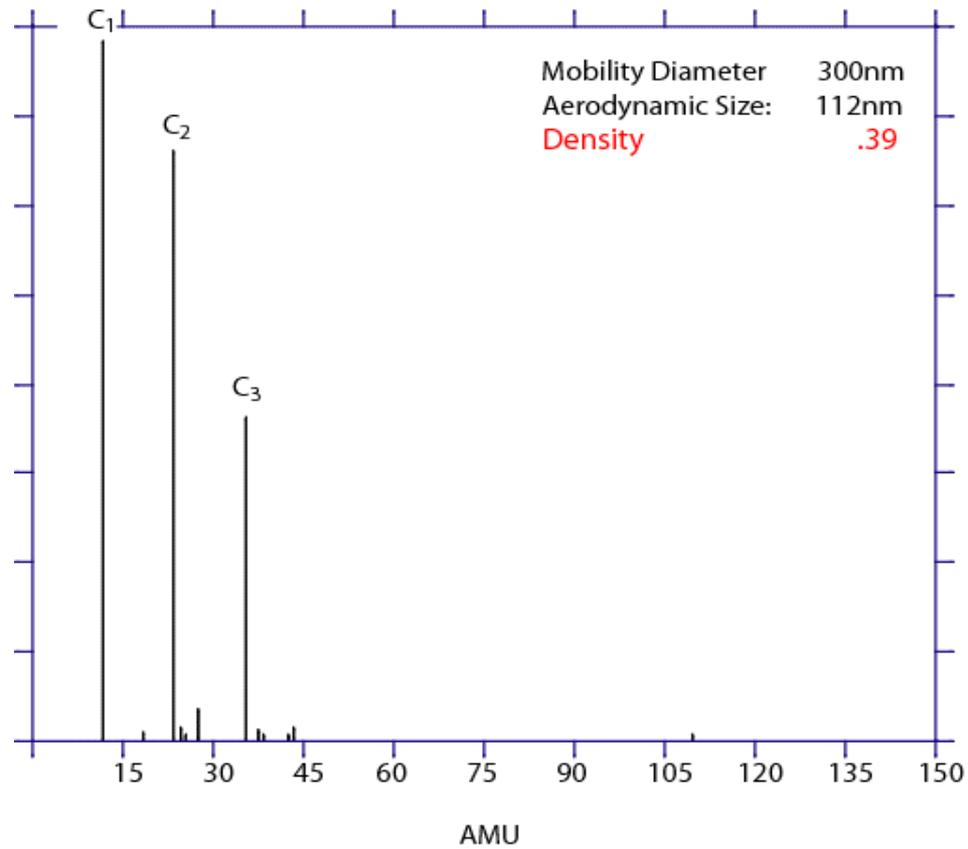
# Particle Density Depends on Composition

## SOOT

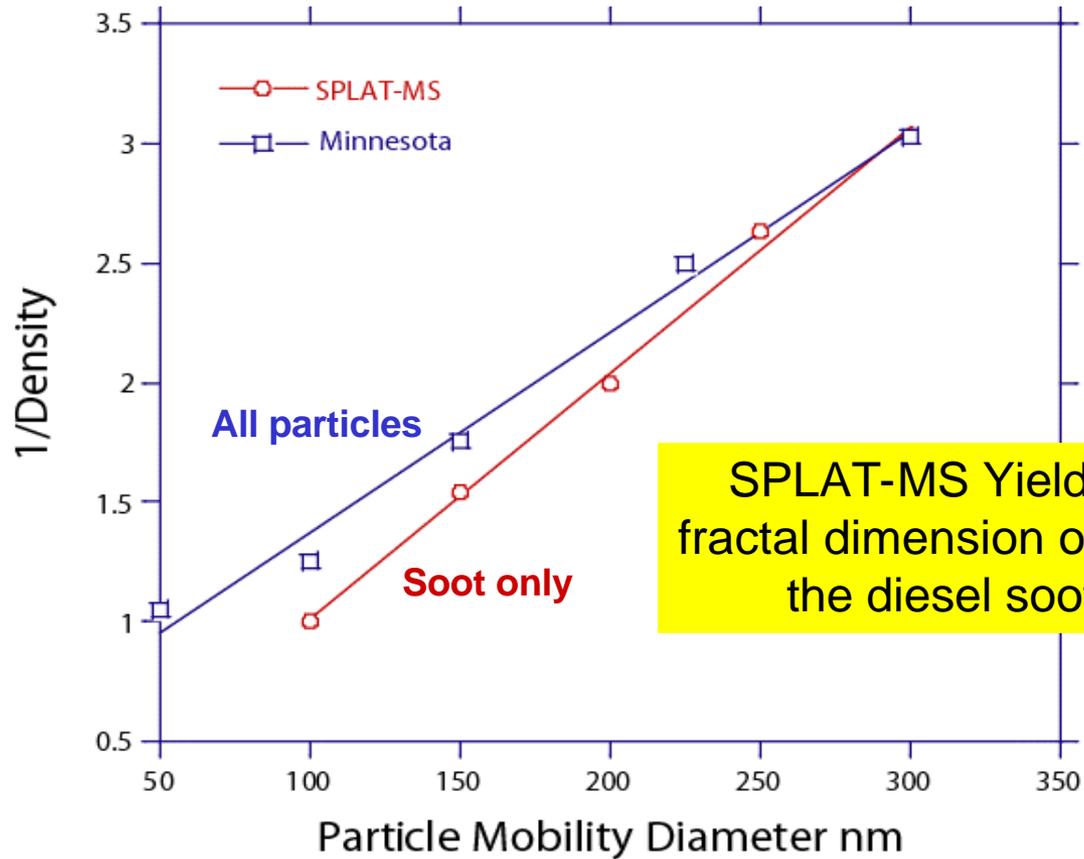


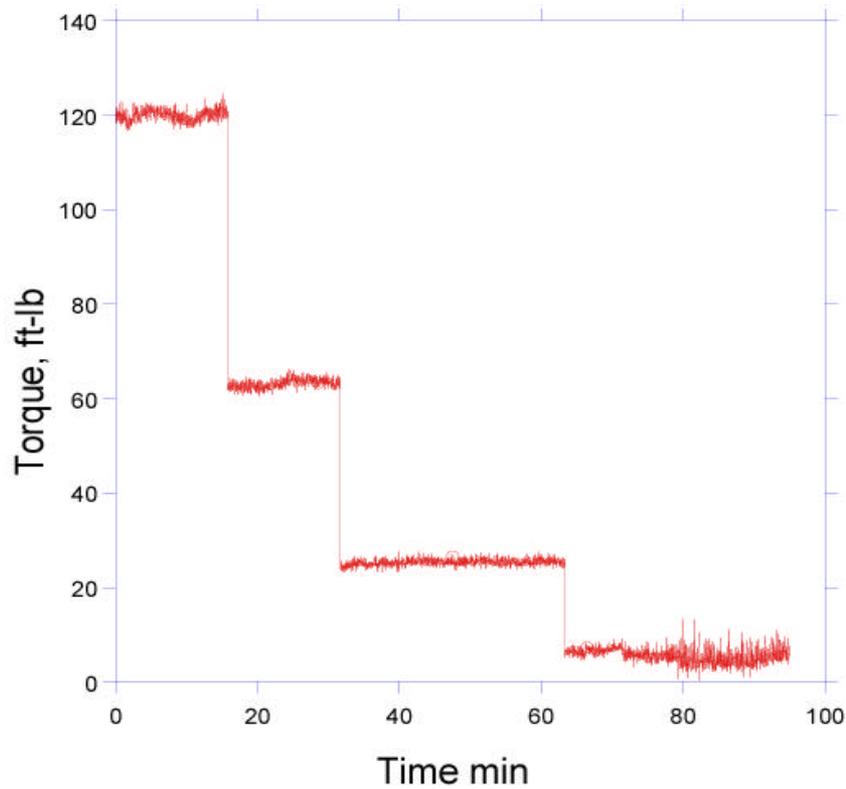
# Particle Density Depends on Composition and Size!!

## SOOT



# Size vs. Density Relationship for Soot Particles

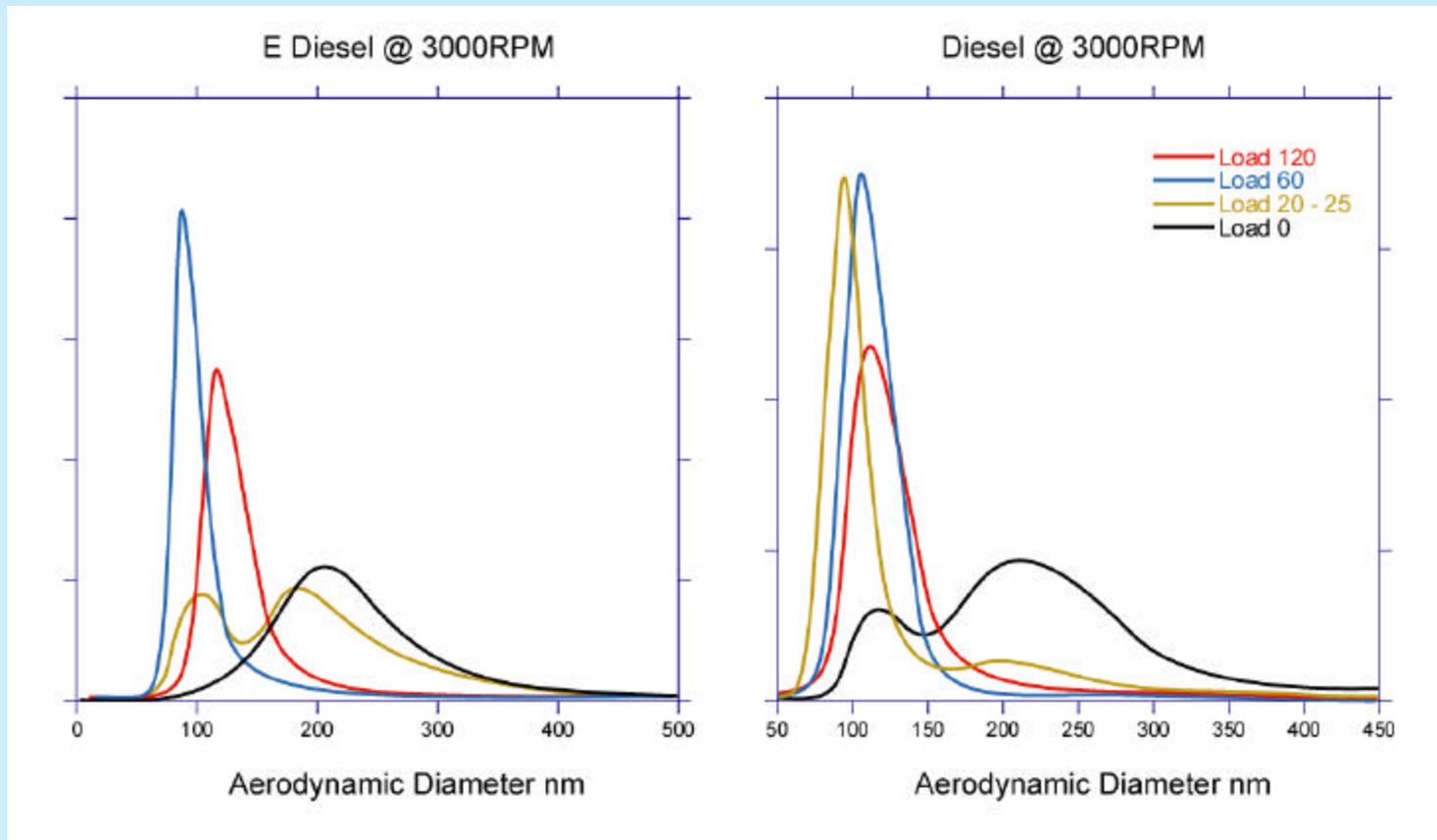




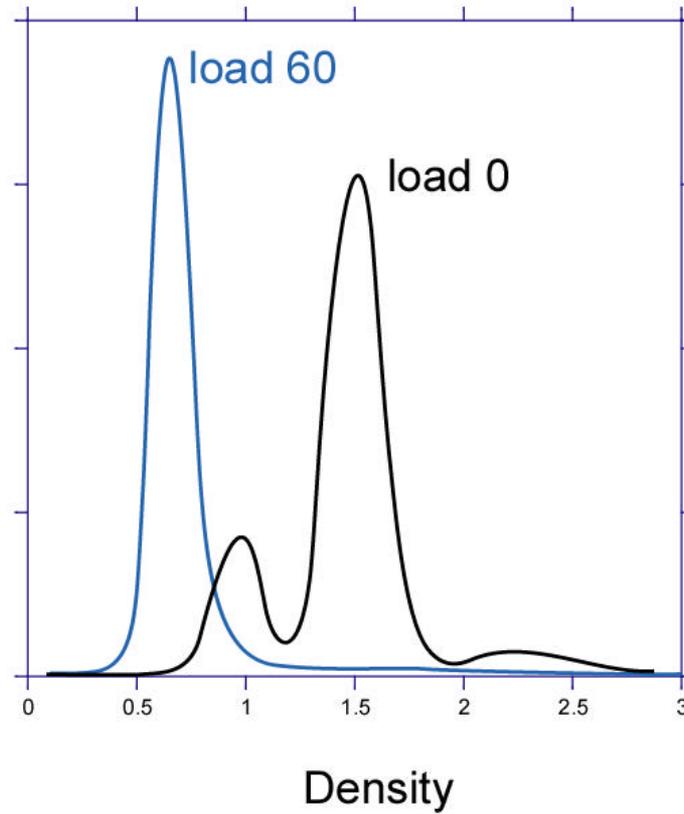
**PM Composition  
and Density as a  
Function of  
Load @ 3000RPM**

# PM as a Function of Load @ 3000 RPM

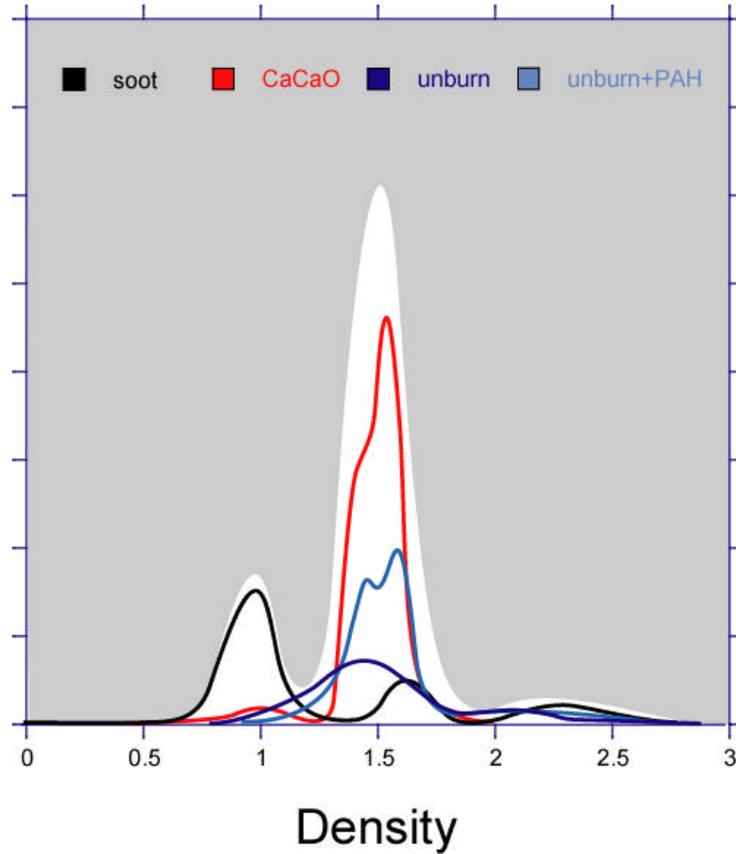
## Aerodynamic Diameter



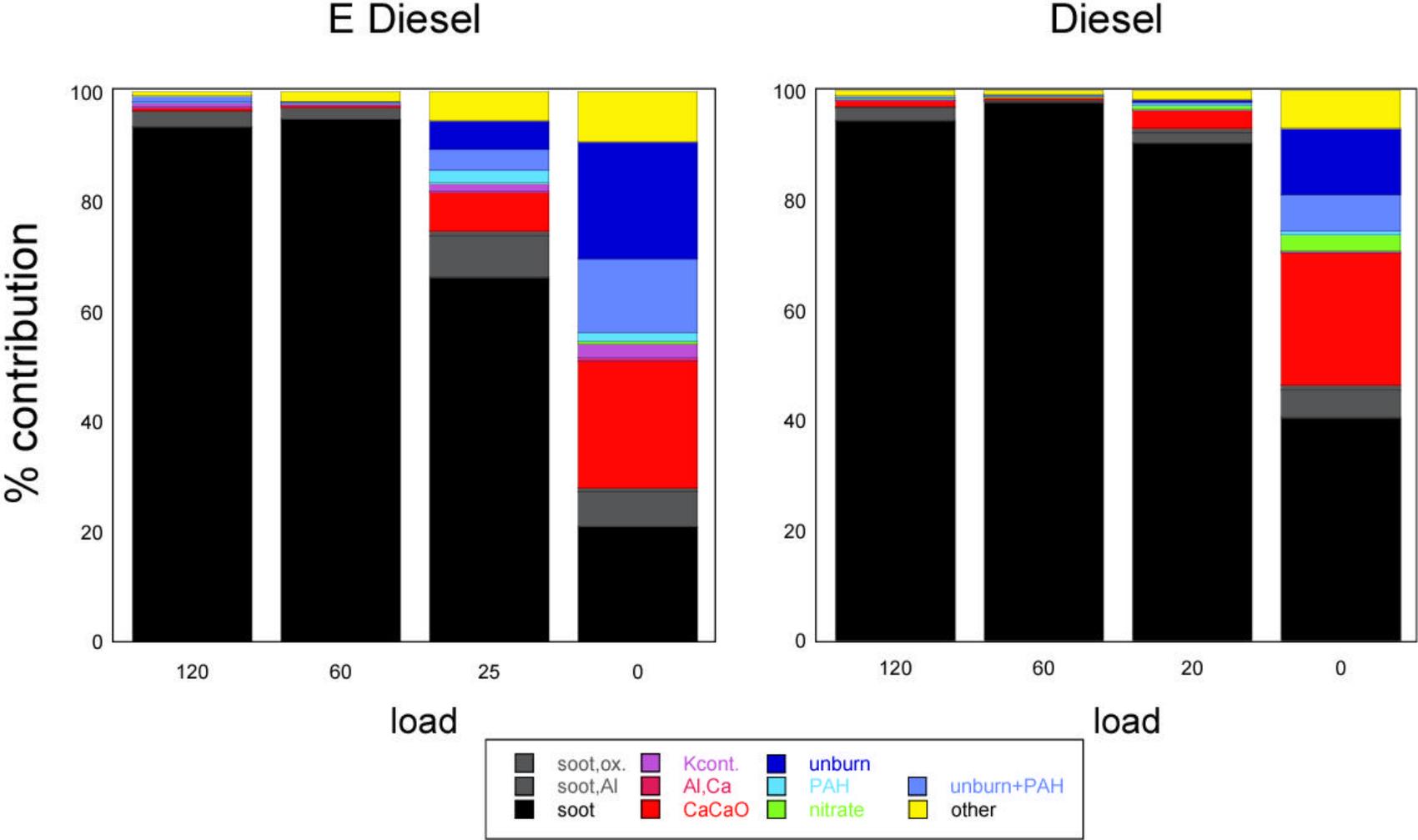
# Engine as a Function of Load @ 3000 RPM



# Engine as a Function of Load @ High RPM

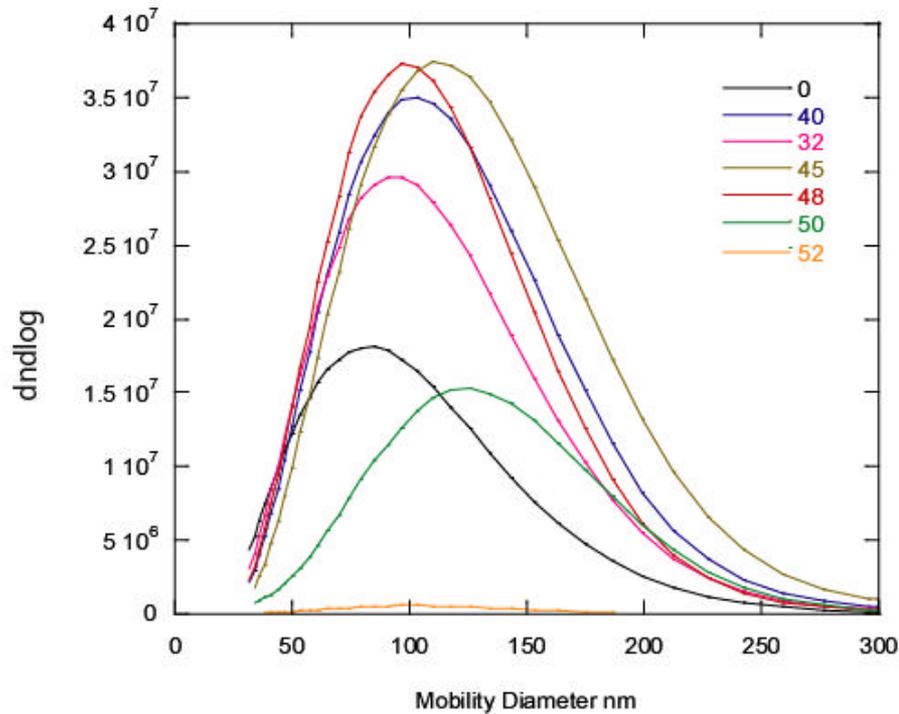


# Engine as a Function of Load @ High RPM

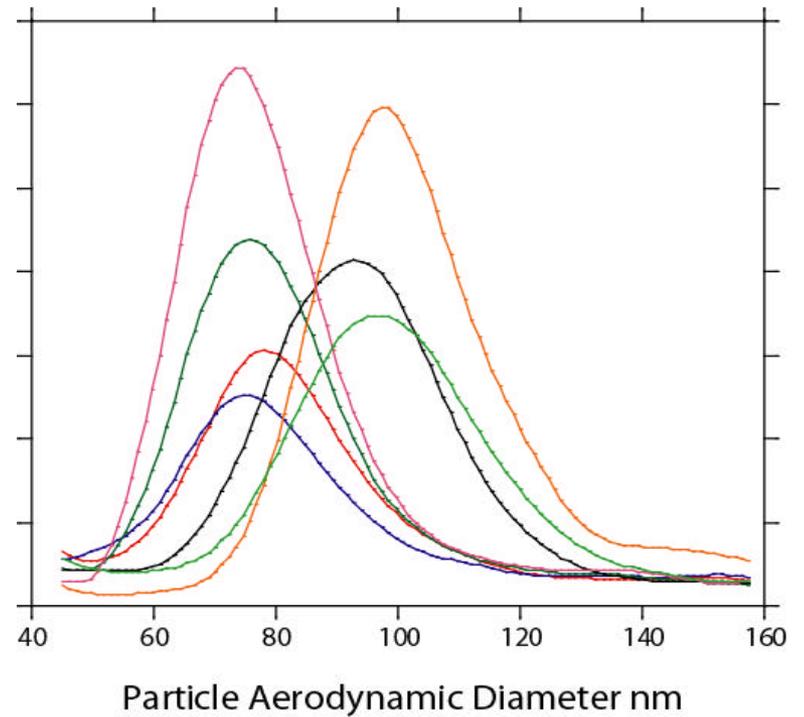


# Particle Number Concentration and Size vs. EGR

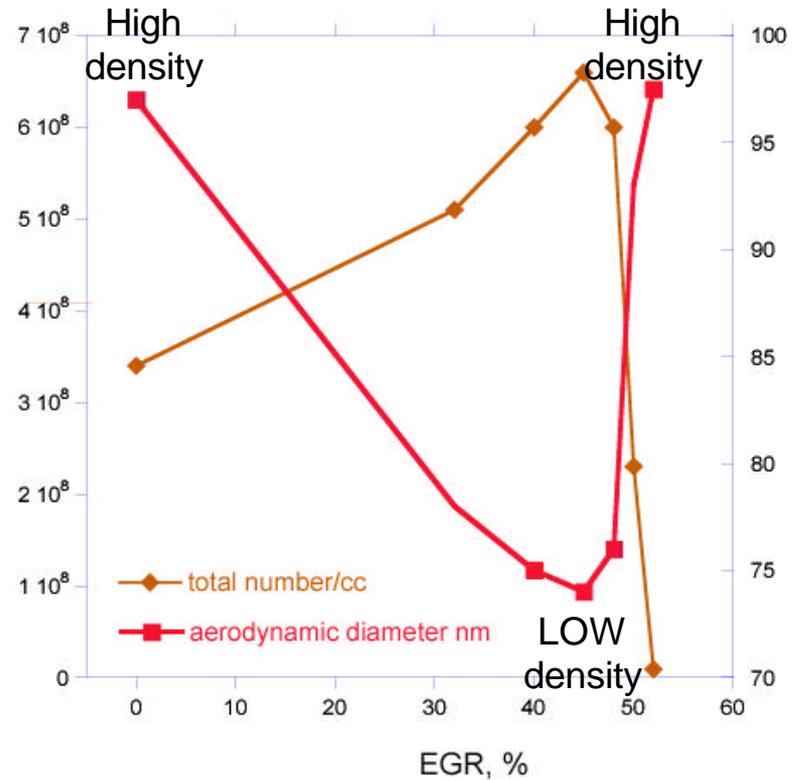
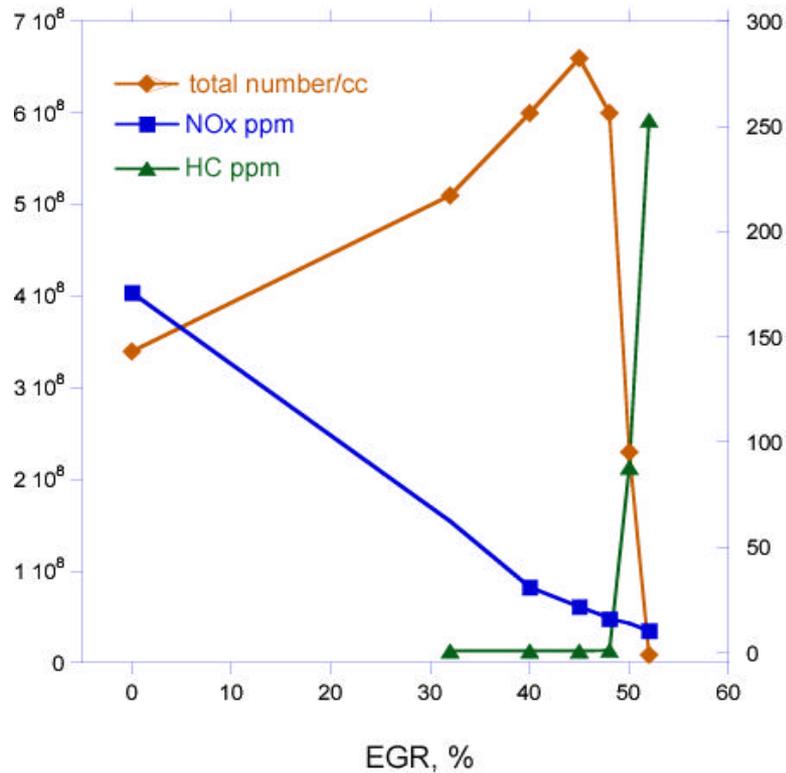
## Mobility size distributions



## SPLAT size distributions



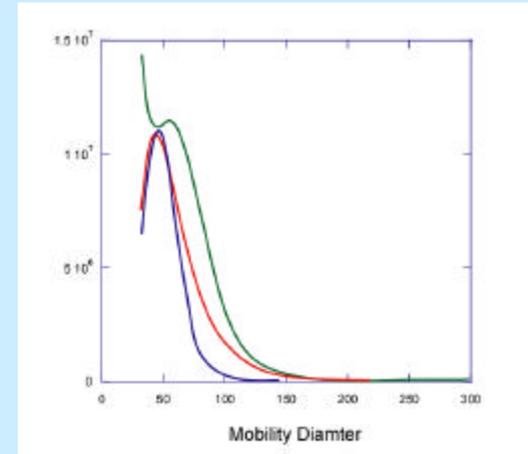
# Particle Number Concentration and Aerodynamic Size vs. EGR



# Where do We Go From Here: The New SPLAT

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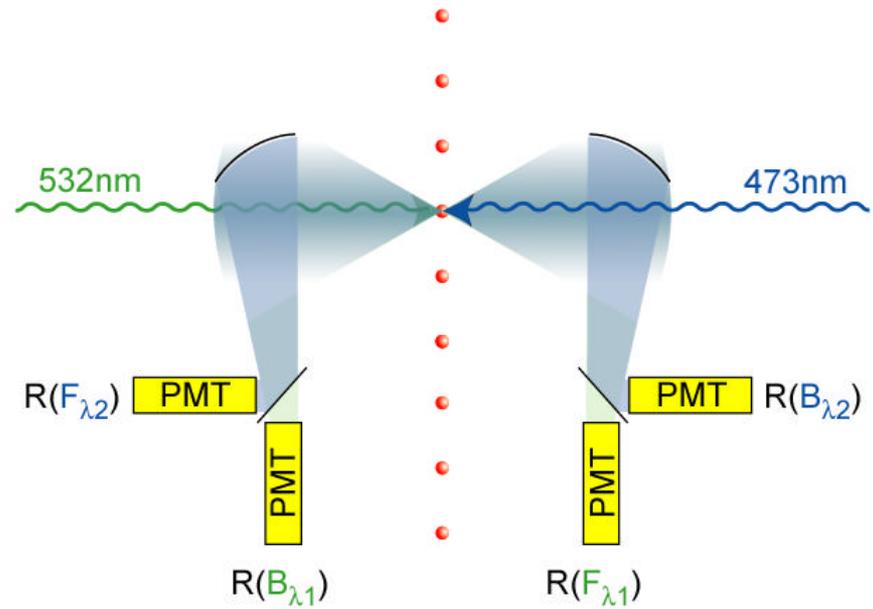
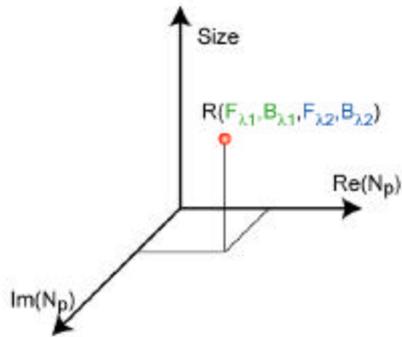
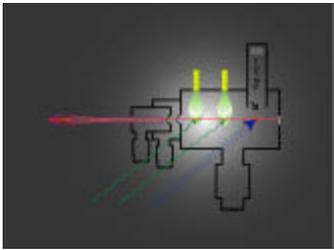
Smaller particles (30nm)



Replace the **Green** laser with **UV**

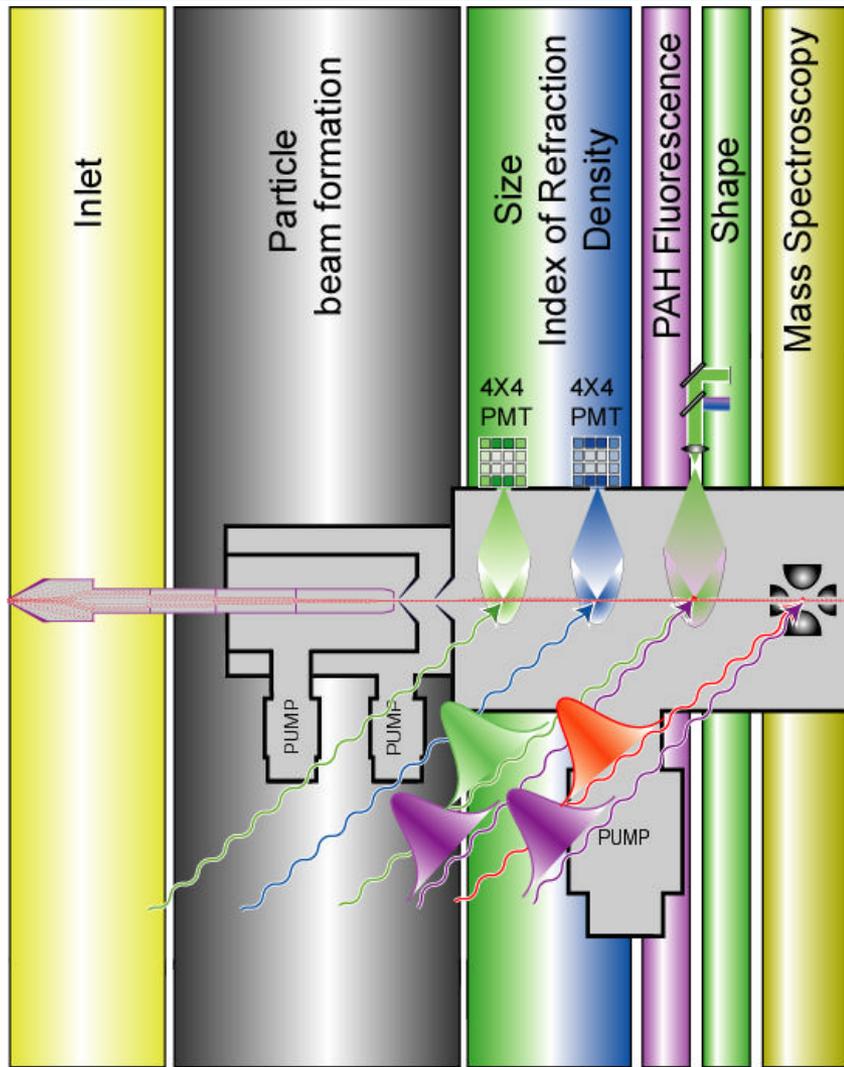
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# Effective Density, and Optical Properties Without DMA

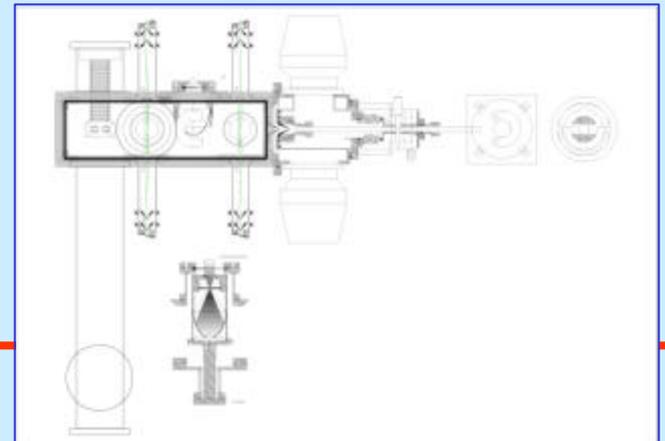


Two color angle resolved light scattering (Szymanski et al. 2002)

# New SPLAT



1. **Aerodynamic size**
2. **Index of refraction**
3. **Density**
4. **Shape**
5. **Incandescence (soot)**
6. **Composition IR + UV**
7. **Composition IR + CI**



# Tailpipe Emissions Comprehensive Characterization

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## Going Back to NTRC

- **SPLAT** - Single particle, size, composition, optical properties, density
  - **AMS** - Semi-volatile in particle phase size resolved
  - **SEM**- Single particle microscopy, composition, chemistry
  - **Cell Exposure** - Proteomics
-

# Conclusion

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- SPLAT-MS provides in real-time individual particle:
    - ▶ **Size** – 40nm to 3micron
    - ▶ **Composition** - IR evaporation followed by UV ionization
    - ▶ **Density** – size and composition resolved
  - SPLAT-MS makes it possible to monitor engine performance in real-time by watching the computer screen
  - SpectraMiner is a powerful tool for detailed data analysis
  - All particles are internally mixed but there are clear classes
  - Particle size, and composition are a strong function of engine operation
  - Density of soot is inversely proportional to size
  - Non soot particles have higher aerodynamic diameter
  - PAHs are found in particles with unburned fuel, and with soot
-